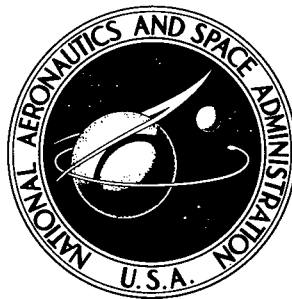


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FROM 0.5 TO 120 ATMOSPHERES)

by *Kenneth J. Bowles and Louis Rosenblum*

Lewis Research Center

Cleveland, Ohio

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VAPOR PRESSURE OF SODIUM FROM 0.5 TO 120 ATMOSPHERES

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SUMMARY

The vapor pressure of sodium was measured by a static capsule method from 0.5 to 120 atmospheres. An equation, $\log p = 4.51961 - \frac{5202.12}{T}$, where p is pressure in atmospheres and T is temperature in $^{\circ}\text{K}$, was fitted to the data with a standard deviation in p of 3.2 percent. This equation was pooled with equations determined in three previous independent studies. The pooled equation, $\log p_p = 4.54025 - \frac{5242.11}{T}$, probably offers the most accurate representation of the vapor pressure of sodium from 0.5 to 120 atmospheres.

INTRODUCTION

The potential use of sodium (Na) as a heat transfer and thermodynamic working fluid in nuclear space power systems (ref. 1) has highlighted the need for accurate vapor-pressure data in the region above 1 atmosphere.

^{stand}
^{here} Vapor-pressure curves for sodium in various ranges above 1 atmosphere have been obtained by several investigators, each using a different experimental method: Makansi, Muendel, and Selke, 0.047 to 6.489 atmospheres (ref. 2); Kirillov and Grachev, 0.2 to 15.4 atmospheres (ref. 3); Ewing, et al., 1 to 25 atmospheres (ref. 4); and Sowa, 1 to 25 atmospheres (ref. 5). Up to 6 atmospheres, there is good agreement within experimental error among the data of references 2, 4, and 5. However, the only determinations from 6 to 25 atmospheres (refs. 4 and 5) show marked divergence. Kirillov's vapor-pressure data are generally low and show little agreement with other investigators' results.

For the past several years, a static capsule method has been used at the Lewis Research Center to measure the vapor pressure of liquid metals. Preliminary results with sodium have already been reported (ref. 6). The final results obtained for sodium from 0.5 to 120 atmospheres will be presented herein, and these results will be compared with those of other investigations.

→ to Summary

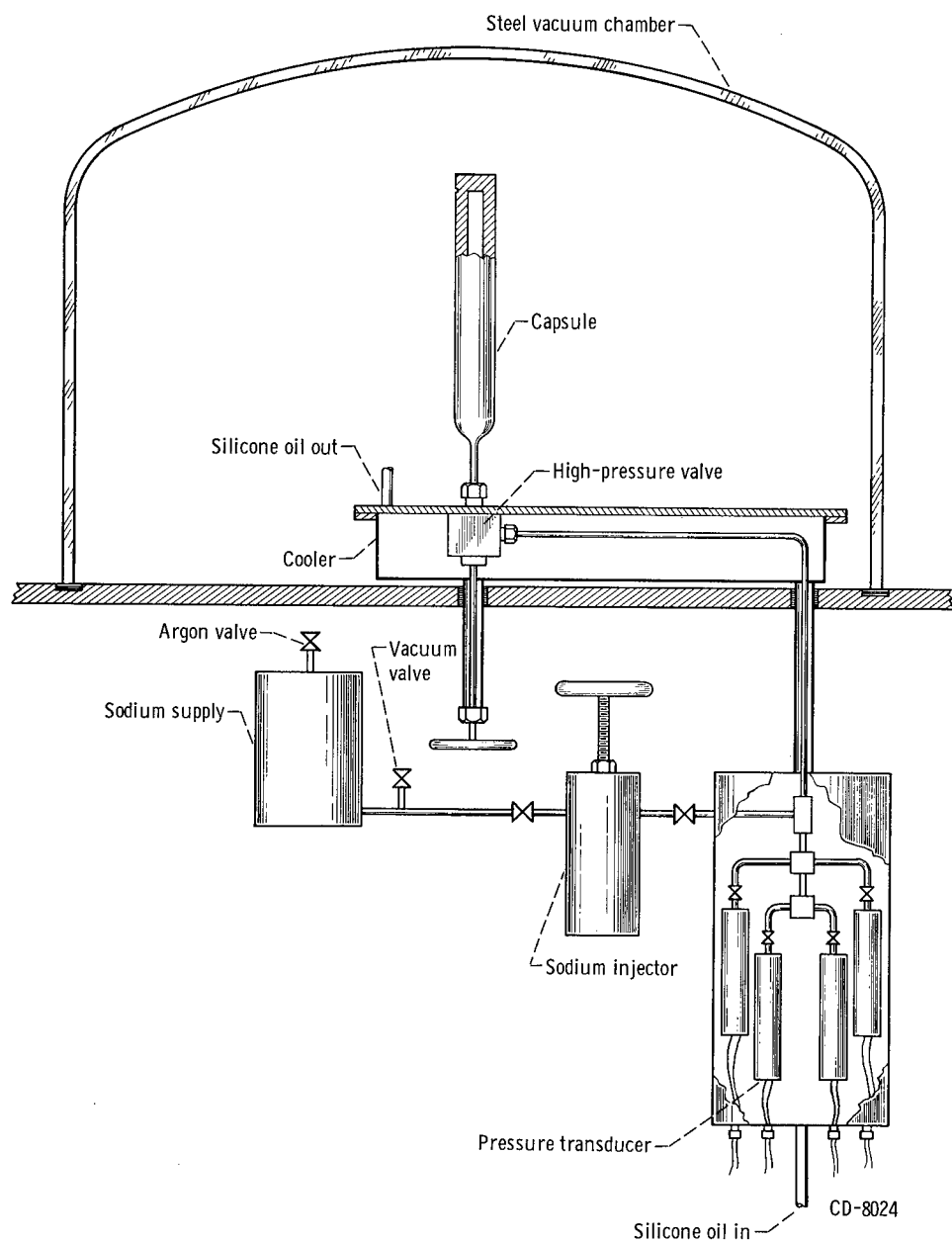


Figure 1. - Apparatus for measuring high-temperature vapor pressure of sodium.

EXPERIMENT

The method used to determine the vapor pressure of sodium consisted of heating a quantity of sodium in a closed capsule and measuring the pressure produced at various temperatures.

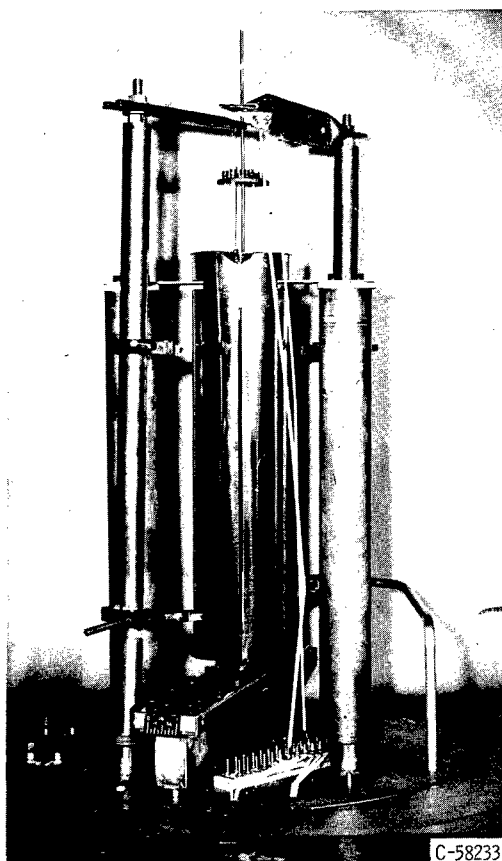


Figure 2. - Capsule, heater, and shield assembly.

Apparatus

The apparatus for measuring vapor pressure is shown in figure 1. The capsule was made of an alloy of 90 percent tantalum and 10 percent tungsten and was 25.4 centimeters long, 2.54 centimeters in outside diameter, and 1.77 centimeters in inside diameter. A capillary tube 8.9 centimeters long, 0.32 centimeter in outside diameter, and 0.25 centimeter in inside diameter welded into the bottom of the capsule served to introduce sodium into the capsule and to transmit the pressure generated in the capsule to an external pressure-measuring device. A tungsten resistance heater

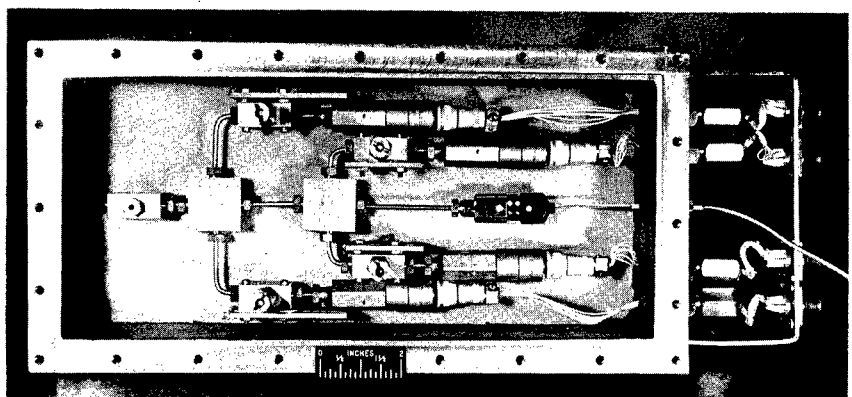
(not shown in fig. 1) was positioned concentrically around the capsule and extended 3.8 centimeters beyond both ends of the capsule. The capsule and heater were totally enclosed by a series of tantalum heat shields (fig. 2). A 20-kilovolt-ampere autotransformer supplied the electric power for the heater.

A steel vacuum bell jar was placed around this capsule assembly. This bell jar was provided with external cooling coils and an optical sight port for viewing the capsule.

The capillary tube from the capsule was connected by a standard compression seal to a stainless-steel high-pressure angle valve. The valve stem was lengthened to extend through the cooler and the vacuum-chamber base plate and thus permit valve operation from outside the chamber.

A high-pressure stainless-steel capillary tube connected the angle valve and a five-branched pressure-measuring manifold. Each of four branches led through a high-pressure valve and terminated in a pressure transducer (fig. 3). Silicone oil was pumped through the pressure transducer enclosure and around the connecting tube and angle valve to maintain a constant temperature of 120°C throughout this portion of the system.

The remaining branch line of the manifold ran through a valve to the sodium injector, which was a 0 to 15 000 pound per square inch manually operated hydraulic pressure in-



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Figure 3. - Pressure-measurement assembly.

tensifier with a special Buna-N packing. The injector had an internal working volume of 27 milliliters and was calibrated so that displacement of the piston could be measured to 0.01 milliliter. The injector was immersed in a silicone oil bath also maintained at 120° C.

A stainless-steel sodium storage tank holding about 1 pound of sodium was connected through a valve to a second port in the injector. (See section Sodium purification.) Purge lines for vacuum and argon were joined to the system at appropriate places.

Procedure

The injector oil bath and the circulating oil were brought up to 120° C, and the capsule and storage tank were heated to a temperature above the melting point of sodium. The entire vapor-pressure apparatus was evacuated to a pressure of 10^{-4} torr. Sodium from the storage tank was forced over with argon pressure to fill the injector, and a measured amount of sodium was injected into the system. The capsule was then heated to a series of test temperatures. Sufficient time was allotted between increases or decreases in temperature to allow the capsule and its contents to reach an equilibrium temperature.

Temperature measurements. - Chromel-alumel thermocouples were used to measure temperatures in run 1; tungsten-rhenium (W-Re) thermocouples were used for runs 2 to 4; and platinum - platinum-13-percent-rhodium (Pt - Pt-13Rh) thermocouples were used in run 5. The Pt - Pt-13Rh thermocouples were calibrated against an NBS standardized Pt - Pt-13Rh thermocouple. The W-Re thermocouples were calibrated against a Pt - Pt-13Rh thermocouple from 845° to 1820° K. Extrapolation of this calibration curve from 1820° to 2200° K gave a deviation of not more than 6° K from the W-Re electromotive force against temperature data of Lachman and McGurty (ref. 7). The

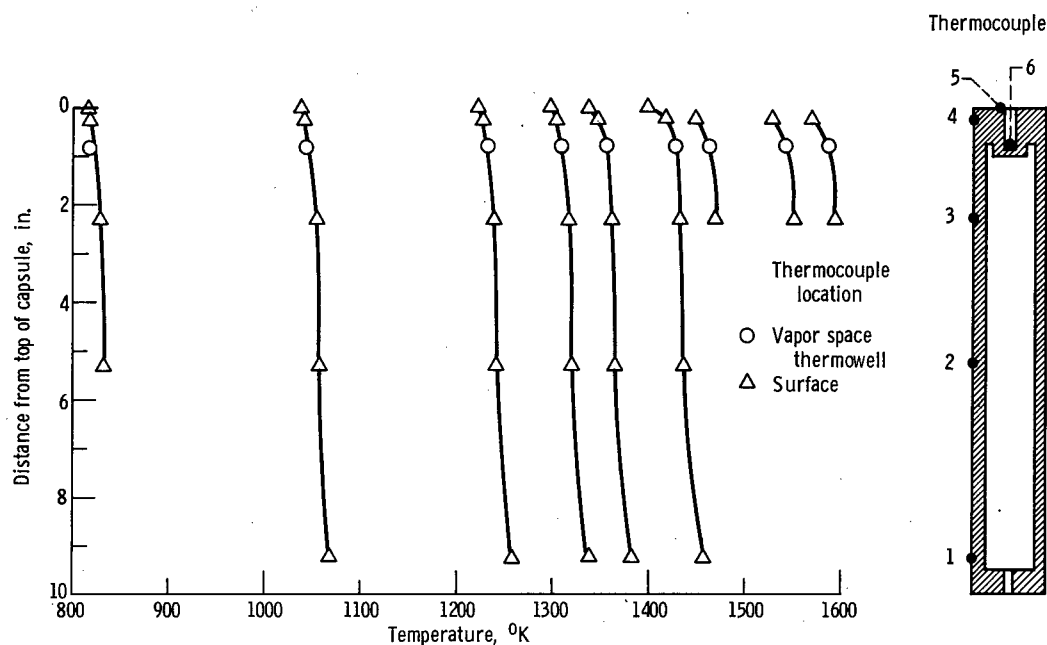


Figure 4. - Temperature profile of vapor-pressure capsule.

accuracy of all temperature measurements on the Kelvin scale is estimated to be within ± 0.25 percent.

Design of the capsule heater and heat-shield assembly ensured that the lower portion of the capsule would be at a slightly higher temperature than the upper end; thus sodium vaporized in the bottom section of the capsule cavity and condensed in the upper. In runs 1 to 4, the thermocouples were located in surface depressions or in holes drilled in the upper end of the capsule. The temperature measured by the thermocouple positioned on the wall radially in line with the upper end of the capsule cavity was considered to be representative of the saturation temperature. In run 5, a modified capsule was used with a heavy-walled thermowell, which extended 0.80 centimeter below the top surface of the capsule cavity. The temperature indicated by the thermocouple located in this thermowell was taken as the saturation temperature.

In a trial test, the temperatures along the capsule outer wall were compared with the temperature in the thermowell (fig. 4). For temperatures above about 1200°K , the temperature of the thermowell was the same as that of the outer wall radially in line with it; for temperatures below 1200°K , the thermowell temperature was lower than the wall temperature. Only one datum point (table I, run 4) was taken below 1200°K with a wall thermocouple. An appropriate correction was applied to this point by consideration of the temperature data shown in figure 4.

Pressure measurements. - Vapor-pressure measurements were made in runs 1 to 4 with pressure transducers that covered a range from 0 to 680 atmospheres in four overlapping ranges: 0 to 238, 0 to 340, 0 to 544, and 0 to 680 atmospheres. Each transducer

TABLE I. - SODIUM VAPOR PRESSURES

Temperature, T, °K	1/T, 1/°K	Pressure, p, atm	Temperature, T, °K	1/T, 1/°K	Pressure, p, atm
Run 1			Run 4		
1416	7.06×10^{-4}	7.28	1414	7.07×10^{-4}	7.15
1441	6.94	8.13	1543	6.48	14.58
1454	6.88	8.76	1689	5.90	27.93
1472	6.80	9.52	1839	5.44	49.99
1290	7.75	2.96	1967	5.09	73.46
Run 2			2043	4.89	94.24
1320	7.58×10^{-4}	3.78	2146	4.66	121.05
1448	6.90	8.34	Run 5		
1505	6.64	11.20	1072	9.33×10^{-4}	0.490
1672	5.98	25.50	1095	9.13	.559
1741	5.74	33.30	1127	8.87	.798
1795	5.57	41.27	1170	8.57	1.134
1852	5.40	49.90	1232	8.12	2.043
1904	5.25	58.90	1262	7.93	2.559
1954	5.12	71.90	1329	7.53	4.030
1994	5.01	79.70	1347	7.43	4.622
2048	4.88	94.60	1404	7.12	6.606
2076	4.81	106.00	1433	6.98	7.939
Run 3			1455	6.87	8.974
1436	6.96×10^{-4}	7.31	1522	6.57	12.920
1503	6.65	10.88			
1585	6.31	17.55			
1672	5.98	26.39			
1734	5.77	33.54			
1794	5.60	43.88			
1870	5.35	57.21			
1930	5.18	71.97			
2004	4.99	84.90			
2041	4.90	94.83			
2071	4.83	102.65			
2111	4.74	110.75			
2154	4.64	120.41			

was calibrated over its entire range at 120° C with a standard dead weight piston gage. The estimated accuracy of the pressure measurements in these runs is ±0.12 atmosphere up to 50 atmospheres and ±0.40 atmosphere over 50 atmospheres.

In run 5, saturation pressures were measured with two pressure transducers, 0 to 3.4 and 0 to 34 atmospheres, calibrated at 120° C with a standard dead weight piston gage. The estimated accuracy of the pressure measurements using these transducers is ±0.013 and ±0.06 atmosphere, respectively.

Sodium purification. - As-received chemically pure sodium was filtered through a 20-micron stainless-steel filter, hot gettered with titanium, and vacuum distilled into stainless-steel storage containers. Over a 2-year period, this supply was used in runs 1 to 5. Analysis of several containers of sodium, 1 to 2 years after purification, gave oxygen contents ranging from 50 to 100 parts per million.

RESULTS AND DISCUSSION

Table I lists the results of the five vapor-pressure runs in which a total of 49 data points were obtained. Two vapor-pressure equations, the three-constant Kirchoff equation and the two-constant integrated Clausius-Clapeyron equation, were fitted to these data by the method of least squares. The latter equation is chosen for presentation herein, since it offers a simpler representation of the data with no significant increase in curve fitting uncertainty:

$$\log p = 4.51961 - \frac{5202.12}{T} \quad (1)$$

where p is the pressure in atmospheres and T is the temperature in °K. The standard deviation in p as calculated from this equation is 3.2 percent. A semilog plot of this equation as p against $1/T$, together with the experimental points, is shown in figure 5.

The integrated Clausius-Clapeyron equation was not expected to provide a good fit for the data, since the assumptions made in deriving the equation are valid only over a limited range of temperature and at low pressures (ref. 8). It has been recently demonstrated theoretically (ref. 9), however, that the errors due to the limitations in the assumptions made in developing this equation may cancel one another.

The errors in the vapor-pressure measurements resulting from impurities in the sodium are believed to be negligible. The predominant impurities are most likely sodium oxide (Na_2O) at low temperatures and tantalum (Ta) at high temperatures. If 100 parts per million is used as the maximum value for oxygen in the sodium and the solution is assumed to obey Raoult's Law, the decrease in vapor pressure due to the presence of

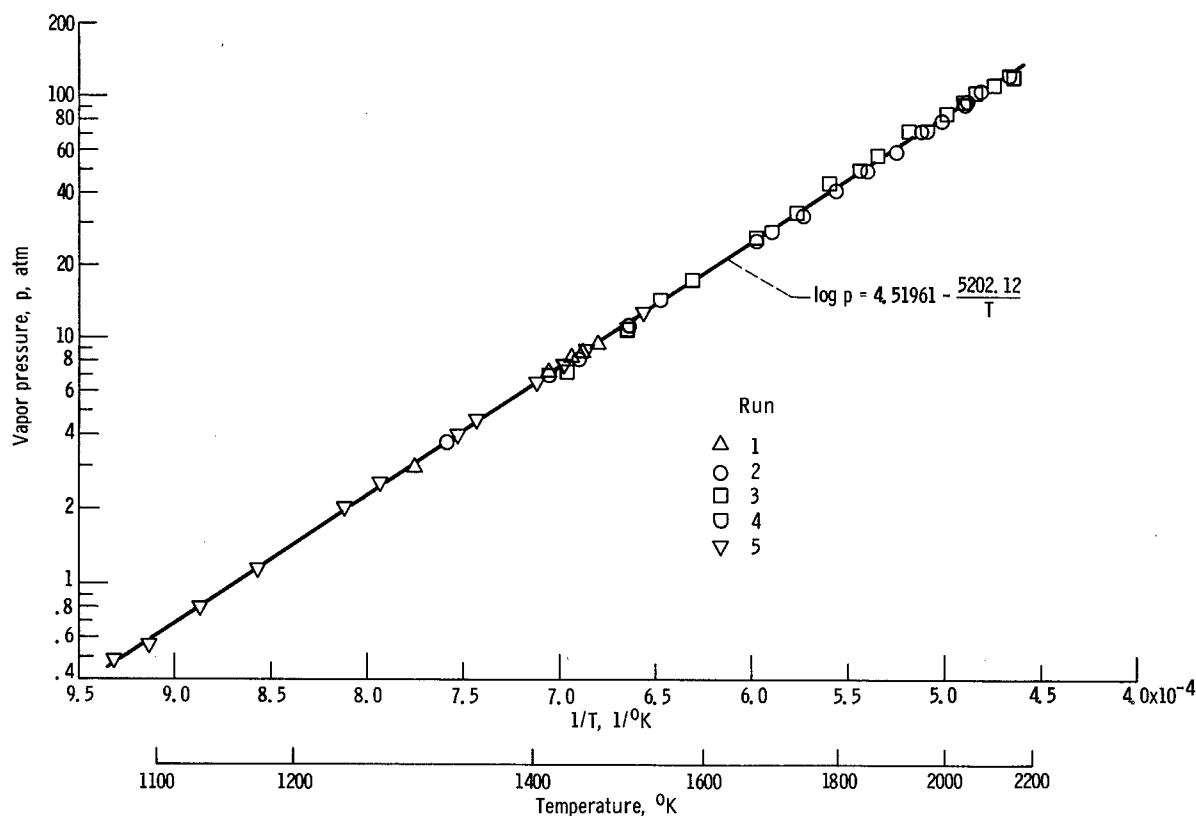


Figure 5. - Vapor pressure of sodium.

Na_2O was calculated to be 0.01 percent. Solubility data for Ta are exiguous; however, an extrapolation to 2000°K of three data points (taken over a range of 598° to 798°K , ref. 10) gives a value of about 10^4 parts per million for the solubility of Ta in Na. If Raoult's Law is used, the decrease in sodium vapor pressure due to the presence of dissolved Ta at 2000°K is calculated to be 0.1 percent.

The vapor-pressure equation determined in this study, equation (1), the equations of references 2 and 4, and the regression equation that was calculated from the data presented in reference 5 were pooled to generate a single curve. Each vapor-pressure equation was solved for p at integral intervals of the value $1/T \times 10^{-4}$ from 6 to 9, and then the regression equation was found in the form of $\log p = A + B/T$ that best fit these values. The pooled equation,

$$\log p_p = 4.54025 - \frac{5242.11}{T} \quad (2)$$

where p_p is in atmospheres, has a standard deviation in p_p of 1.6 percent. A graphical comparison of the experimental vapor-pressure - temperature relations is shown in figure 6. The abscissa is given as temperature in $^\circ\text{K}$, and the ordinate is expressed as

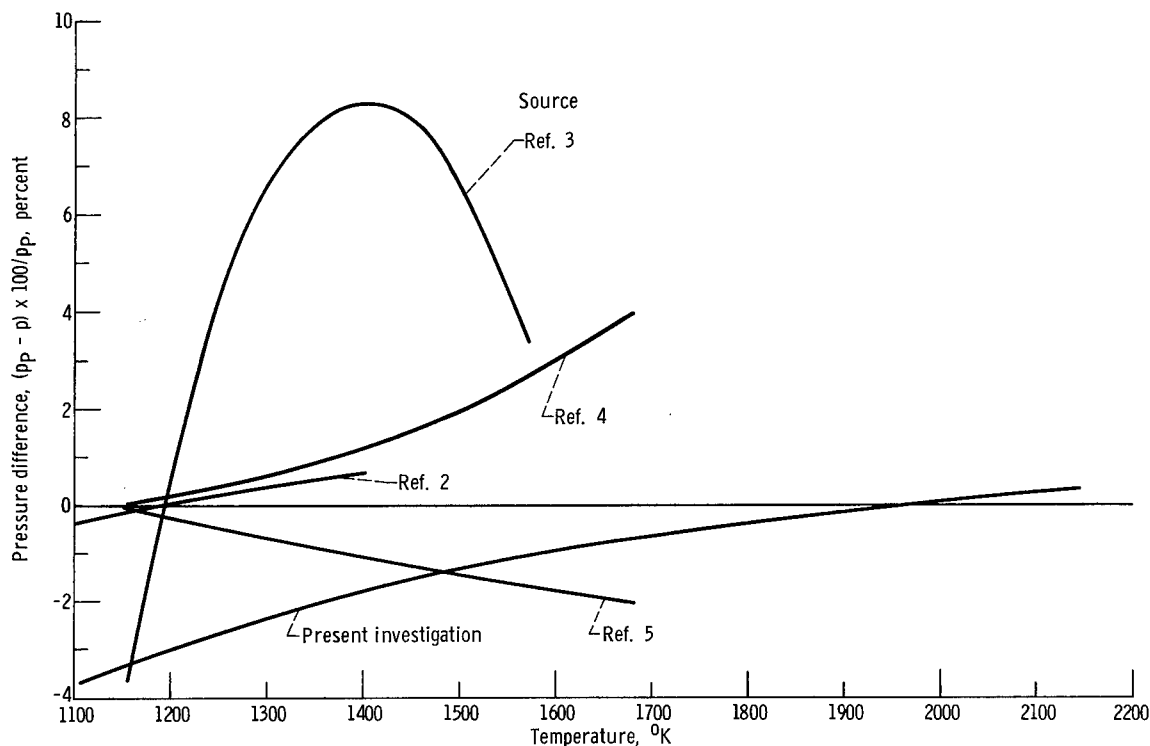


Figure 6. - Comparison of vapor-pressure data for sodium.

$(p_p - p) \times 100/p_p$ or the percent difference in vapor pressure between pooled vapor-pressure values (eq. (2)) and the vapor pressure calculated from an individual investigator's vapor-pressure curve. Each curve of percent difference covers only the temperature range of the respective vapor-pressure determination.

A percent difference curve derived from the vapor-pressure data of Kirillov and Grachev (ref. 3) is included in figure 6. The wide discrepancy between Kirillov and Grachev's data and the data used to generate p_p permits the rejection of the bulk of their data with a confidence of better than 99.7 percent.

As is evident in figure 6 and as can be inferred from the small value of the standard error of estimate in p_p of 1.6 percent, the agreement among the vapor-pressure curves is good. This agreement is all the more striking because different experimental vapor-pressure methods were used in each investigation. Equation (2) probably offers the most accurate representation of the vapor pressure of sodium from 0.5 to 120 atmospheres.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 10, 1965.

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